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Correlations between chemical composition and provenance of Justino site ceramics by INAA

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Instrumental neutron activation analysis (INAA), have been used for the definition of compositional groups of potteries from Justino site, Brazil, according to the chemical similarities of ceramic paste. The outliers were identified by means of robust Mahalanobis distance. The temper effect in the ceramic paste was studied by means of modified Mahalanobis filter. The results were interpreted by means of cluster, principal components, and discriminant analyses. This work provides contributions for the reconstruction of the prehistory of baixo São Francisco region, and for the reconstitution of the Brazilian Northeast ceramist population of general frame.

Introduction

Nowadays archaeology uses a variety of methods and tools to reconstruct ancient cultures. These methods include excavation, environmental analysis, sociology, scientific and historical dating methods, historic and iconographic source, and material analysis of the found artifacts to name just a few.[1] Since ceramics represent a sophisticated merging of previously separate domains of human knowledge and experience, these objects are intensively studied by means of archaeometric methods around the world.[2,3] Visual properties such as shape and surface decoration are frequently used as cultural and chronological indicators. In addition, microscopic properties such as paste texture (i.e., the clay and temper combination) can be used to study preparation techniques. The chemical composition can be used to locate the source(s) of ingredients or to provide evidence of geographic displacement. Oxidation state of iron-bearing constituents can be used to reconstruct firing conditions. Trace elements present at concentrations below 1000 ppm usually provide the best information for provenance studies.[4]

Recent studies have been conducted in the ancient ceramist culture of the Xingó region, situated in Canindé do São Francisco, about 150 km from Aracaju, Sergipe State, in the Brazilian Northeast. Figure 1, showed the existence of an independent ceramist group, a group producing and using ceramics, not related to the Tupiguarani and Aratu group, well established in the region.[5] Dating obtained by means of ^{14}C indicates that there is an evidence of human occupation of 8,980 years BP (Beta 86745) in Xingó region.

This work aims to contribute to the understanding of the Baixo São Francisco River occupation dynamics by means of compositional study of ceramic samples from Justino site, the main archaeological site in the area. For this, 76 ceramic fragments (cemeteries: A 25, B 26 and C 25) and one clay sample were analyzed by means of INAA.

Experimental

Archaeological background

Chronology studies of ceramist occupation at Justino site accomplished by thermo-luminescence and radiocarbon dating, showed a chronology amplitude from 5.570 to 1.280 BP. According to this study, the ceramist occupation in Xingó area is one of the oldest in Brazilian Northeast. Four human occupations were identified at Justino site. They were called Cemetery A: 1280±45 to 2530±70 BP, Cemetery B: 2650±150 to 3270±135 BP, Cemetery C: 4790±80 to 5570±70 BP and Cemetery D: approximately 8950±70 BP. The first three cemeteries correspond to ceramist farmer groups and the last cemetery corresponds to hunter – collector groups.[6]

A categorization of social hierarchies as well as a distinction between sexes and ages were performed in several of the burial sites in Cemeteries A, B and C. These distinctions were not observed in Cemetery D.[6] Xingó communities had burial rituals in areas previously chosen and each individual was given a different mortuary complement to define social structures of the ceramist groups in the area.[6] It was observed that the associations between the vestiges and burials showed characteristics of hunter – collector groups, which

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indicates changes from hunter – collector to ceramist culture, with more evidence in Cemetery B. In cemetery A, these distinctions were observed more clearly for older individuals.[6]

Sample preparation and measurements

Ceramic powder samples were obtained by cleaning the outer surface and drilling to a depth of 1–2 cm using a variable speed drill with a tungsten carbide rotary file attached to the end of a flexible shaft. Depending on the thickness, 3 or 5 holes were drilled as deep into the core of the fragment as possible without drilling through the walls. Finally, the powered samples were dried in an oven at 105 °C for 24 hours and stored in desiccators. The analytical procedure for the analysis of pottery samples was published elsewhere.[7,8]

Statistical method

Various methods for detecting outliers have been studied, which are related, mainly, to Mahalanobis distance.[9,10] Mahalanobis distance is defined for a sample $x_1, \ldots, x_n$ of n observations in the p-dimensional real space R^p as:

$$d^2 = [(x_i - T)^t C^{-1}(x_i - T)]^{1/2} \text{ for } i = 1, ..., n \quad (1)$$

where t is the transpose matrix, T and C are location and covariance estimators, respectively. In the case of multivariate normal distribution, the arithmetic mean and the sample covariance matrix are the best choices. In this case, d^2 approximated to a chi-square distribution χ_p^2 with p degrees of freedom. In general, data points with d^2 higher than the cut-off value are considered potential outliers.

However, arithmetic mean and sample covariance matrix are sensitive to outlying observations. Thus, the Mahalanobis distance needs to be estimated by a robust procedure. Several robust estimators to C and T in Eq. (1), have been proposed in the literature such as estimators of multivariate location and dispersion that include the minimum covariance determinant (MCD).[11,12]

The aim of MCD is to find a subset of size h, objects with the smallest determinant of the covariance matrix.[13] As a compromise between robustness and efficiency, a value of $h \approx 0.75n$ (n is the sample size) is frequently used. Using robust estimators of location and scattering in Eq. (1) leads to the so-called robust distances (RDs). If a square RD for a case is larger than $\chi^2_{p;0.98}$, it can be declared an outlier candidate.

To identify outliers in this work, the data set was submitted to principal component analysis to reduce the dimensionality of the set. After that it was possible to construct the ellipse corresponding to the squared Mahalanobis distance equal to $\chi^2_{2;0.98}$. The sample found outside of the tolerance ellipse, in the space established for the first two principal components, was considered outlier.[13]

To help in the creation of compositional group a principal component analysis (PCA) was performed on the INAA data, since PCA is a convenient way to capture and view complex multidimensional data. PCA is a technique used to reduce multidimensional data sets to lower dimensions for analysis. In PCA, the data set is transformed on the basis of eigenvector method to determine the magnitude and direction of maximum variance of the data set distribution.[14] By means of PCA it is expected that plots of the first few principal components reveal the data structure. This fact facilitates quick identification of variables, responsible for the differences between case groups in compositional studies. In addition, plots of two and/or three dimensions from PCA can be used to recognize sample compositional groups.[14]

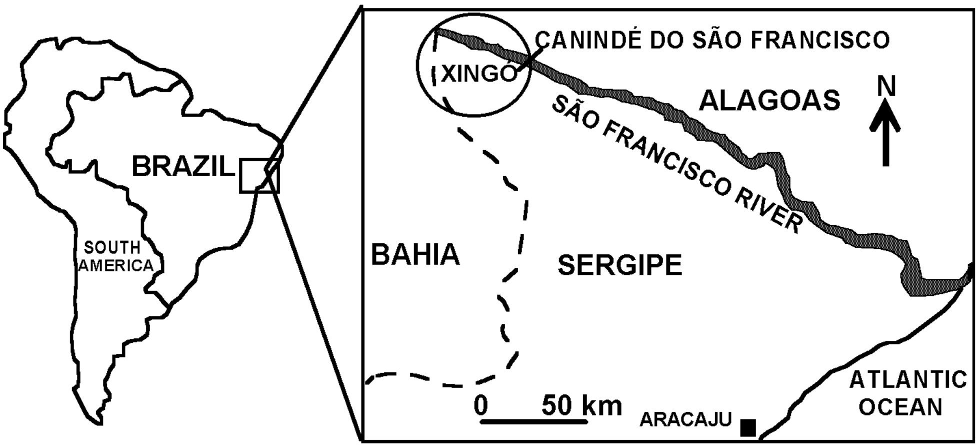

Fig. 1. Study area localization map

Two other statistical methods were applied on the data set: cluster and discriminant analysis. Cluster analysis is a general term that applies to a variety of specific techniques but the essential components are:

(a) a measure of the similarity-dissimilarity between specimens which are defined and

(b) a clustering algorithm specified for group specimens on the basis of the defined measure.

To identify initial groups of samples from Justino site, a cluster analysis was performed using Ward's method and squared Euclidian distance.[15]

Discriminant analysis is a widely applied multivariate statistical technique used in archaeometry to identify elements which are most useful to discriminate and to graphically display the chemical distinction among these groups.[16] Discriminant analysis was used in this work to statistically distinguish the samples from Cemeteries B and C.

Dilution effect correction

Considering the modified Mahalanobis distance (d^2) as the distance between a single sample $\vec{X}$ and centroid of the group $\vec{Y}$, d^2 is given by:

$$d^2(\vec{X},\vec{Y}) = \frac{1}{m}\left[{}^t(f\vec{X}-\vec{Y})(f^2S_X+S_Y)^{-1}(f\vec{X}-\vec{Y})\right] \quad (2)$$

where S_Y is a covariance matrix, S_X an uncertainty matrix and

$$f = \frac{\phi_Y}{\phi_X}$$

is called the dilution factor. By multiplying $\vec{X}$ by f, a correction takes place.[17]

Under the assumption that a correction for dilution should bring together a data point $\vec{X}$ and a center point $\vec{Y}$ as close as possible, f can be calculated as solution of

$$\frac{\partial}{\partial f}\left[{}^t(f\vec{X}-\vec{Y})(f^2S_X+S_Y)(f\vec{X}-\vec{Y})\right]=0 \quad (3)$$

A better resolution in grouping is achieved after dilution correction.[17] Every correction can be done by using the Search Program, which was developed by Dr. Hans MOMMSEN and his Archaeometry Group at Bonn University. This program performs a number of useful tasks in pottery grouping according to element concentration data.

Results and discussion

One of the basic requirements underlying the compositional characterization of the archeological pottery is that analytical technique presents adequate precision. Elements with low precision can reduce the discriminating effects of other well-measured elements. These differences can be used to form ceramic compositional groups because vessels manufactured from a given clay source will be more similar to other type of vessels which were manufactured from a different source. To evaluate the analytical process and to establish the chemical elements which can be used in the data interpretation, the elemental concentrations for reference material Brick Clay – NIST-SRM-679 were statistically compared with the data found in our laboratory. Several elements presented relative standard deviation, RSD, less than 10%, similar to those from the literature.[18] In this work all the elements with RSD less than 10% were considered.[19] The interference of ^{235}U fission in the determination of La, Ce and Nd was negligible because U concentrations did not exceed 5 ppm and rare earth concentrations were not very low.[14]

Zn presented an RSD less than 10% but was not excluded from the data set because its determination suffers strong gamma-ray interferences of ^{46}Sc. Although Co and Ta had RSD smaller than 10% they were not included because their concentrations can be affected by tungsten carbides drills.[20] Ce was removed from the data set because samples showed high variability, which can be related to characteristics of ionic-exchange of the Ce with elements present in clays.[21] Based on these screening criteria 11 elements: Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Sc, Yb and Th were used for result interpretation.

Initially, the results were transformed to $\log_{10}$ to compensate for the large magnitude difference between the measured elements at trace level and the larger ones. The $\log_{10}$ transformation of the data before a multivariate statistical method are common. One reason for this is the belief that, within manufactured raw materials, elements have a natural lognormal distribution, and that data normalization is desirable. Another reason is that a logarithmic transformation tends to stabilize the variance of the variable and would, thus, give them approximately equal weight to non standard multivariate statistical analysis.[22] After logarithmic transformation, the data set was submitted to outliers test by means of robust Mahalanobis distance. Four samples from Cemetery A, 3 samples from Cemetery B and 2 samples from Cemetery C were considered outliers. After obtaining the final database, all element concentrations for the studied potteries from the cemetery were corrected according to their dilution factor using Eqs (2) and (3). Table 1 shows the results for mean and spread values for Cemeteries A and B, with and without correction.

Table 1. Composition mean (M) for pottery in Cemeteries B and C

Element	Cemetery B		Cemetery C	
	Without correction (M ± CV)	With correction (f = 1.00 ± 0.03)* (M ± CV)	Without correction (M ± CV)	With correction (f = 0.90 ± 0.08)* (M ± CV)
Na, %	1.55 ± 12.79	1.53 ± 12.43	1.31 ± 23.65	1.27 ± 18.45
Lu	0.68 ± 33.22	0.65 ± 22.76	0.47 ± 39.44	0.44 ± 23.84
Yb	4.54 ± 34.48	4.32 ± 24.20	3.44 ± 47.50	3.16 ± 30.48
La	59.41 ± 24.18	58.13 ± 20.28	48.93 ± 40.44	45.69 ± 29.52
Th	13.53 ± 37.78	13.55 ± 37.35	14.68 ± 53.58	15.27 ± 51.02
Cr	37.96 ± 72.31	39.38 ± 71.44	27.91 ± 52.29	27.13 ± 45.41
Cs	6.71 ± 40.17	6.63 ± 39.91	4.77 ± 60.89	4.49 ± 59.23
Sc	17.57 ± 22.81	17.16 ± 18.68	12.91 ± 43.44	12.06 ± 31.58
Fe, %	5.99 ± 22.88	5.82 ± 14.29	4.44 ± 37.88	4.14 ± 22.82
Eu	2.58 ± 22.03	2.51 ± 15.04	1.85 ± 50.61	1.70 ± 36.97
Hf	7.52 ± 19.88	7.42 ± 18.86	7.06 ± 36.18	6.71 ± 23.42

Values are in ppm, and spread in percentage of the average.
*f represents the mean of the dilution factor with spread.

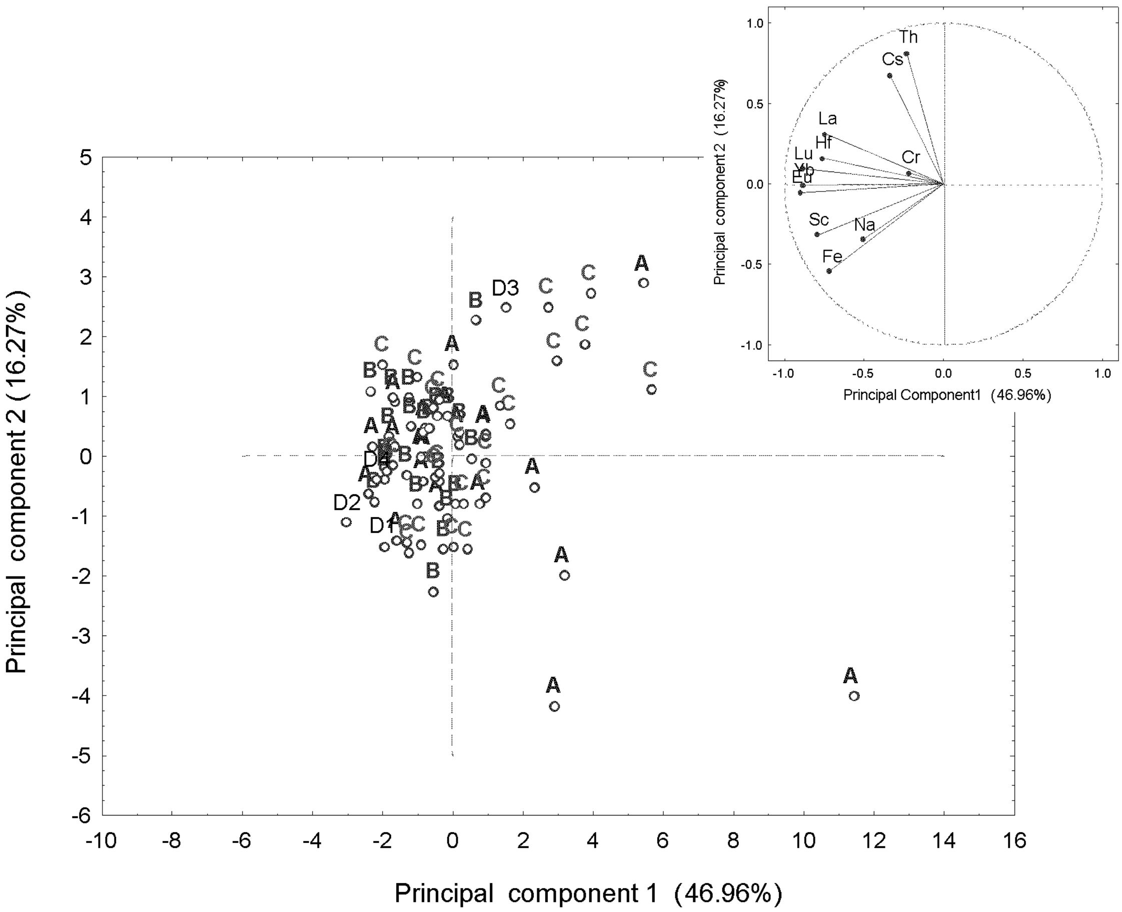

Fig. 2. First and second principal component biplot for Cemeteries A, B and C

PCA indicated that the three first components accounted for the majority of the total variance in the data set, give 74% of total variance. The Kaiser criterion was utilized to obtain this number of principal components.[15] According to the Kaiser criterion 4 principal components can be assumed to explain the variability of the data set.

Examination of space formed by first and second principal components showed that most specimens appeared to fall into a single homogeneous compositional group, corresponding to Cemetery B, and other group most widespread corresponding to pottery samples from Cemetery C. The samples from Cemetery A seemed scattered in the space formed by two first principal components, as shown in Fig. 2. The high dispersion from Cemetery A potteries can be the result of cultural exchanges between ceramist groups which occupied Justino archaeological site in recent periods with others ceramist groups from Xingó area, which influenced the ceramics manufacturing process.

A discriminant analysis, DA, of 46 samples by dilution factor was done to confirm the existence of two different groups of ancient pottery fragments buried at Justino site. This analysis was based on their chemical composition and the fragments of Cemeteries B and C. Figure 3 presents a bivariate plot of discriminant function 1 versus discriminant function 2 showing that two main groups were formed. Figure 3 illustrates that the pottery samples from each Cemetery B and C from Justino site are chemically homogeneous, since they concentrate in an ellipse with a confidence level of 95%. These results illustrate the difference in the raw materials used to manufacture the potteries.

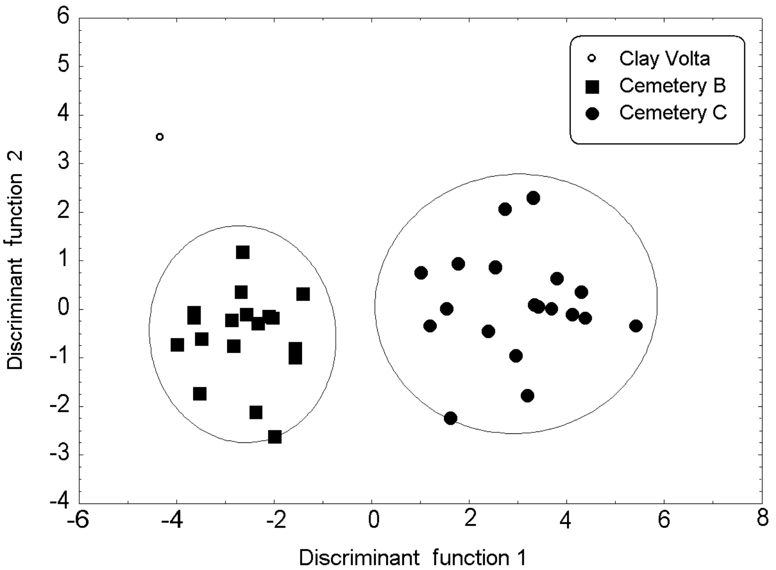

Fig. 3. Linear discriminant analysis data from Cemeteries B and C. Ellipses represent 95% confidence level

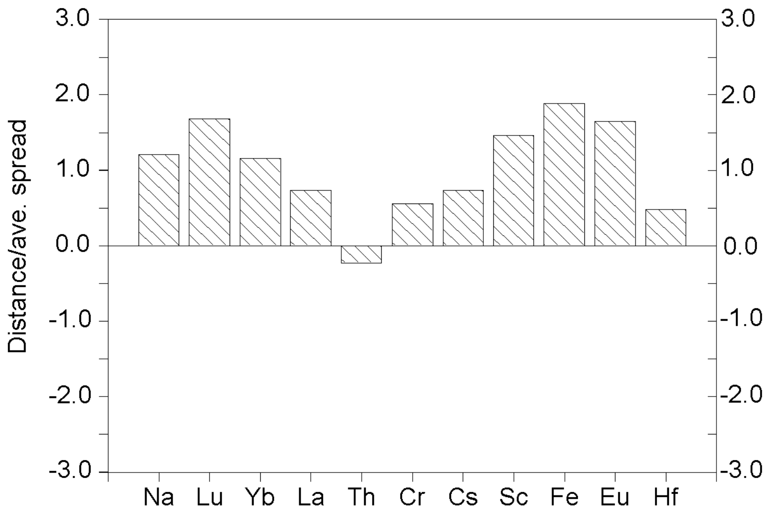

Fig. 4. Standardized differences of the concentration values of the Cemeteries B and C group (in units of the average spreads) for 11 elements

Figure 4 shows the concentration differences between Cemeteries B and C plotted as a bar diagram in units of the average spread values. Differences in Na, Lu, Yb, Sc, Fe and Eu are more evident. It is possible to see that the group of Cemetery B is chemically different from that of Cemetery C, which suggests that different pastes were used.

According to the variability presented for two Cemeteries B and C in Table 1 and Fig. 3, it can be seen that the ceramic paste from Cemetery C is more heterogeneous than that of Cemetery B. Cemetery C was once occupied by an incipient ceramist group, establishing a change from hunter–collector group to ceramist group. Because of this, the variability of the chemical composition of the pottery in this cemetery could be consequence of the technological evolution of the pottery manufacture during this period, indicating an experimentation process in ceramics production. Nevertheless, during the period of Cemetery C occupation, expert craftsmen have kept the know-how to produce potteries with some quality control, mainly, the ceramic paste homogeneity.

Conclusions

The INAA analysis of pottery from Justino site (Cemeteries A, B and C) was successful in identifying distinct groups with various chemical composition. It was verified that samples from Cemetery C were characterized by higher dispersion in the concentrations, which could be the result of the manufacturing process and not of the temper effect. The compositional differences among potteries from the site studied can be understood in terms of cultural influences in the preparation of the ceramic paste, changes in land use and organization of ceramic production or of the availability of raw materials. A systematic collection of clays in the region would reveal its raw material sources. Nowadays, however, this archaeological site is submerged because this area is now part of Xingó hydroelectric power station. The results obtained in this work provided subsidies for hypothesis formulation on the technological evolution of the Xingó area people.

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References

1. R. GEBHARD, Hyperfine Interact., 150 (2003) 1.
2. P. M. RICE, J. Archaeol. Method Theory, 1 (1999) 1.
3. M. T. STARK, J. Archaeol. Res., 11 (2003) 193.
4. P. WEIGAND, G. HARBOTTLE, E. V. SAYRE; in: Exchange Systems in Prehistory, EARLE and J. E. ERICSON (Eds), Academic Press, New York, 1977, p. 15.
5. G. MARTIN, Pré-história do Nordeste do Brasil, 3rd ed. rev., Editora Universitária da UFPE, Recife, 2000, p. 440.
6. M. C. S. VERGNE, O. A. CARVALHO, A. N. QUEIROZ, Rev. Canindé, 4 (2002) 251.
7. C. S. MUNITA, R. P. PAIVA, M. A. ALVES, P. M. S. OLIVEIRA, E. F. MOMOSE. J. Radioanal. Nucl. Chem., 248 (2001) 93.
8. C. S. MUNITA, R. P. PAIVA, P. M. S. OLIVEIRA, E. F. MOMOSE, R. PLÁ, M. MORENO, O. ANDONIE, F. FALABELA, L. MUNOZ, I. J. KOHNENKAMP, J. Trace Microprobe Techn., 19 (2001) 189.
9. K. I. PENNY, Appropriate Critical Values when Testing for a Single Multivariate Outlier by Using the Mahalanobis Distance, in: Applied Statistics, 35, Royal Statistical Society, United Kingdom, 1987, p. 153.
10. P. J. ROUSSEEUW, B. C. VAN ZOMEREN, J. Amer. Stat. Assoc., 85 (1990) 633.
11. J. HARDIN, D. M. ROCKE, J. Comput. Graph. Stat., 14 (2004) 928.
12. A. J. HADI, Roy. Stat. Soc., 54 (1992) 761.
13. P. FILZMOSER, R. G. GARRET, C. REIMANN, Comput. Geosci., 31 (5) (2005) 579.
14. M. D. GLASCOCK, Characterization of Archaeological Ceramics at MURR by Neutron Activation Analysis and Multivariate Statistics, Chemical Characterization of Ceramic Pastes in Archaeology, in: H. NEFF (Ed.), Prehistory Press, Madison, 1992, p. 116.
15. R. A. JOHNSON, D. W. WICHERN, Applied Multivariate Statistical Analysis, 3rd ed., Prentice Hall, New Jersey, 1992.
16. A. BEHARAV, E. NEVO, Genetica, 119 (2003) 259.
17. T. BEIER, H. MOMMSEN, Archaeometry, 36 (1994) 287.
18. C. S. MUNITA, R. P. PAIVA, M. A. ALVES, E. F. MOMOSE, J. Radioanal. Nucl. Chem., 244 (2000) 244.
19. J. O. SANTOS, C. S. MUNITA, M. E. G. VALERIO, C. VERGNE, P. M. S. OLIVEIRA, J. Radioanal. Nucl. Chem., 269 (2) (2006) 441.
20. M. ATTAS, J. M. FOSSEY, Y. YAFFE, Archaeometry, 26(1) (1984) 104.
21. G. W. A. NYAKAIRU, C. KOEBERL, H. KURZWEIL, Geochem. J., 35 (2001) 245.
22. M. D. GLASCOCK, H. NEFF, K. J. VAUGHN, Hyperfine Interact., 154 (2004) 95.